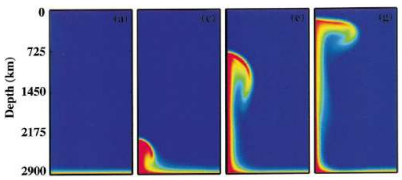
Lattice Dynamics

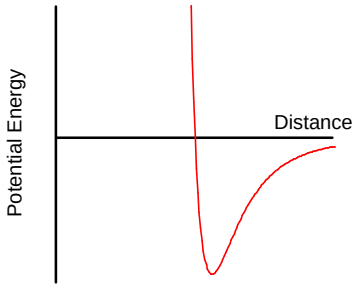
Thermal Expansion

- As temperature changes, density changes
- Thermodynamics
  - Relates this change to changes in other properties
  - Cannot tell the magnitude or even the sign!
- Why positive alpha?
- What value vs. P,T,X?
- Macroscopic to Microscopic
- Thermodynamics to Statistical Mechanics



Interatomic Forces

- Ambient Structure
  - Minimum
- Bulk Modulus
  - Curvature
- Thermal Expansivity
  - Beyond harmonic
  - Molecules
  - Solids



One Dimensional Lattice

$$V_n = V_0 + \frac{1}{2}\sum_{p=-N}^{N}\frac{\partial^2 V_{n,n+p}}{\partial u_n^2}(u_{n+p}-u_n)^2 + H.O.T.$$

$$F_n = -\frac{\partial V_n}{\partial u_n} = \sum_{p=-N}^{N} K_p(u_{n+p}-u_n)$$

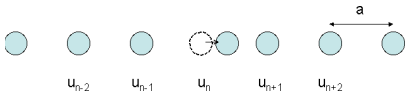
$$K_p = \frac{\partial^2 V_{n,n+p}}{\partial u_n^2}$$

$$m\frac{\partial^2 u_n}{\partial t^2} = \sum_{p=-N}^{N} K_p(u_{n+p}-u_n)$$

$$u_n = u_0 \exp[i(nka-\omega t)]$$

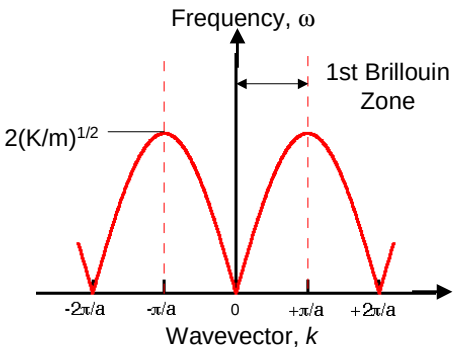
$$\omega^2 = \frac{4}{m}\sum_{p=1}^{N} K_p \sin^2\left(\frac{p\mathbf{k}\bullet\mathbf{a}}{2}\right)$$

$$\omega = 2\sqrt{\frac{K}{m}}\left|\sin\left(\frac{ka}{2}\right)\right|$$



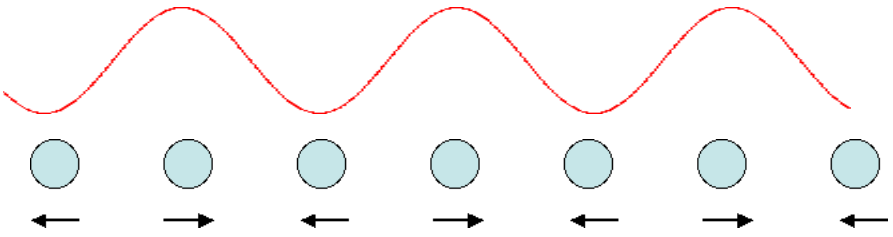
One Dimensional Lattice

- Periodicity reflects that of the lattice
- Brillouin zone center, k=0: ω=0
- Brillouin zone edge, k=π/a: ω=maximum
- All information in first Brillouin zone

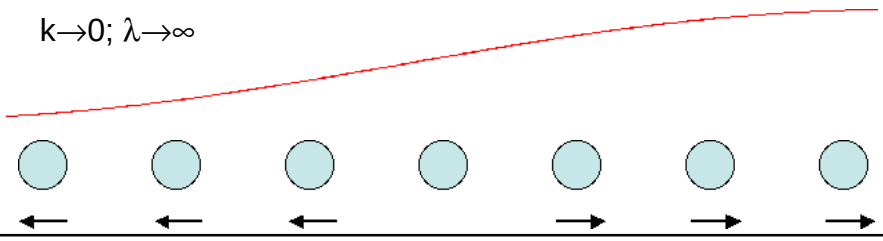


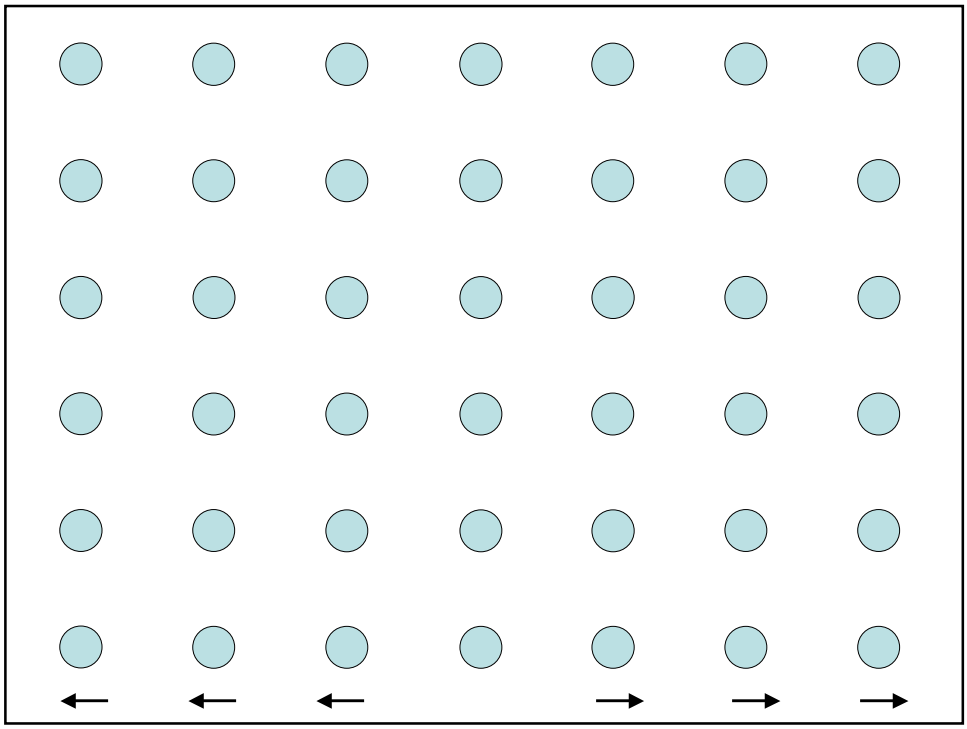
One Dimensional Lattice

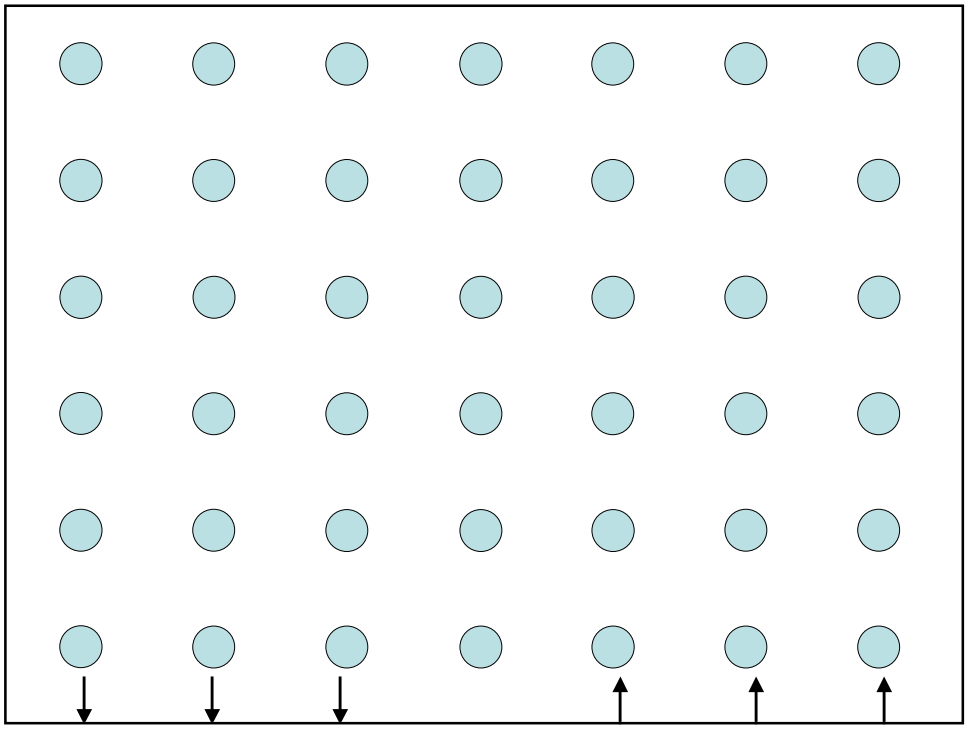
k=π/a=2π/λ; λ=2a



k→0; λ→∞



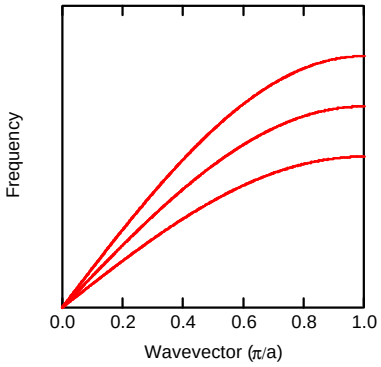




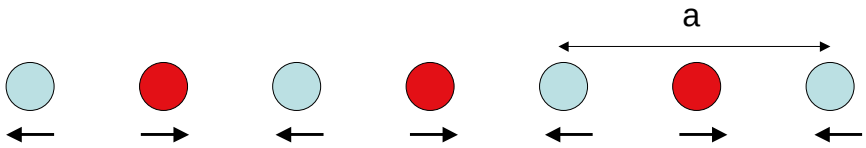
Acoustic Velocities

$$\omega = 2\sqrt{\left|\frac{K}{m}\right|}\sin\left(\frac{ka}{2}\right)$$

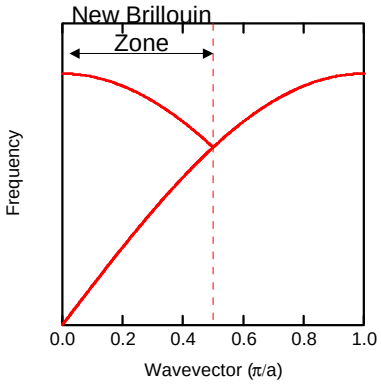
- $k \rightarrow 0$
  $\omega = 2(K/m)^{1/2} ka/2$
  $\omega/k = dw/dk = a(K/m)^{1/2}$
- Acoustic Velocity
  - $v = a(K/m)^{1/2}$
- Three dimensions
  - Wavevector, k_i
  - Polarization vector, p_i
  - For each k_i, 3 acoustic branches
  - $k_i \,||\, p_i$ longitudinal (P) wave
  - $k_i \perp p_i$ transverse (S) waves (2)



Polyatomic Lattice

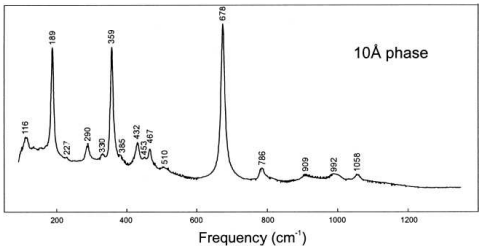


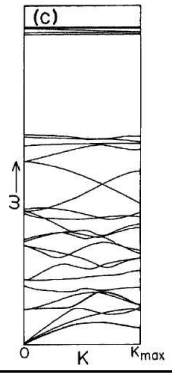
- Unit cell doubled
- Brillouin Zone Halved
- Acoustic Branches folded
- New, finite frequency mode at k=0
- Optic Branch



General Lattice

- Number of modes = 3N organized into 3Z branches
  - Z= number of atoms in unit cell
- 3 Acoustic branches
- 3Z-3 optic branches
- Experimental Probes
  - Optic zone center
    - Raman
    - Infrared
  - Acoustic near zone center
    - Brillouin
  - Full phonon spectrum
    - Inelastic neutron scattering



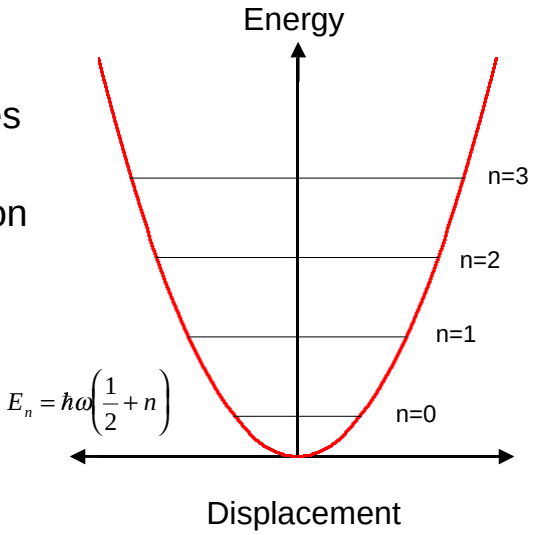


Quartz

$MgSiO_3$ Perovskite Movie

Internal Energy

- Sum over all vibrational modes
- Energy of each mode depends on
  - Frequency
  - Population
    - Frequency
    - Temperature



Heat Capacity

$$U_{vib} = \frac{1}{2}\sum_{i=1}^{3N}\hbar\omega_i + \sum_{i=1}^{3N}\bar{n}_i\hbar\omega_i$$

$$\bar{n}_i = \left[\exp\left(\frac{\hbar\omega_i}{kT}\right)-1\right]^{-1}$$

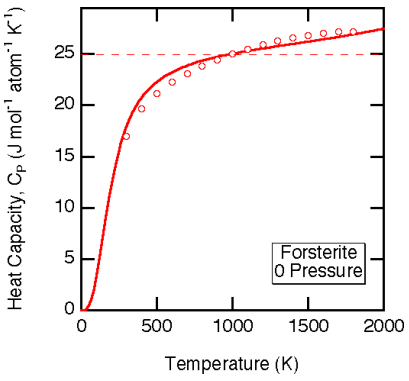
$$U_{vib} = \frac{1}{2}\sum_{i=1}^{3N}\hbar\omega_i + \sum_{i=1}^{3N}\frac{\hbar\omega_i}{\exp\left(\frac{\hbar\omega_i}{kT}\right)-1}$$

High Temperature

$$U_{vib} \approx \frac{1}{2}\sum_{i=1}^{3N}\hbar\omega_i + \sum_{i=1}^{3N}kT$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = 3Nk$$

- or
- C_V=3R per mol of atoms (Dulong-Petit)



Thermal Pressure 1

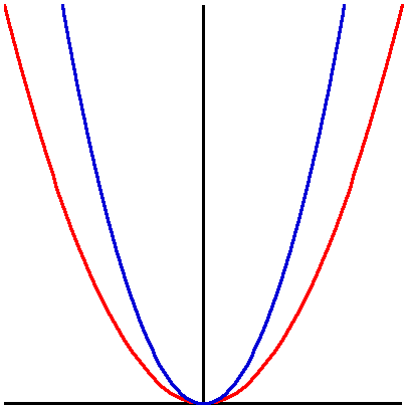
$$F_{TH} = \frac{1}{2}\sum_{i=1}^{3N}\hbar\omega_i + kT\sum_{i=1}^{3N}\ln\left[1-\exp\left(-\frac{\hbar\omega_i}{kT}\right)\right]$$

$$P_{TH} = -\left(\frac{\partial F_{TH}}{\partial V}\right)_T$$

$$P_{TH} = \frac{\gamma}{V}U_{TH}$$

$$\gamma = \sum_{i=1}^{3N}\gamma_i u_i \Big/ \sum_{i=1}^{3N} u_i$$

$$\gamma_i = -\frac{\partial \ln\omega_i}{\partial \ln V}$$



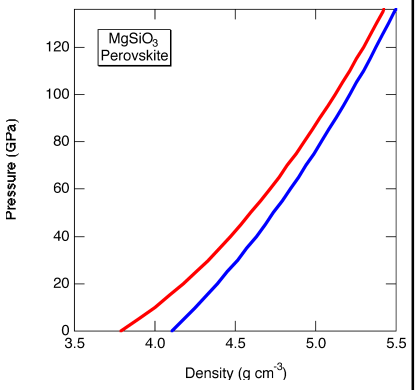
- Compression Increases
  - Vibrational frequencies
  - Vibrational energy
- $\rightarrow$ Thermal pressure

Thermal Pressure 2

$$P_{TH} \approx \gamma\rho 3nRT$$ Thermal Pressure

$$V_B = \left(\frac{\partial P}{\partial \rho}\right)_S = \frac{K_S}{\rho}$$ Bulk Sound Velocity

$$q = -\frac{\partial \ln\gamma}{\partial \ln\rho}$$ Temperature Dependence of V_B



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